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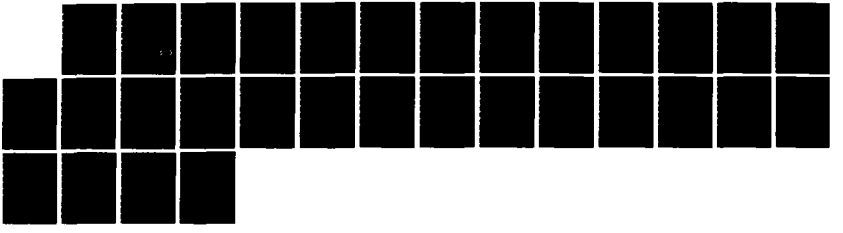

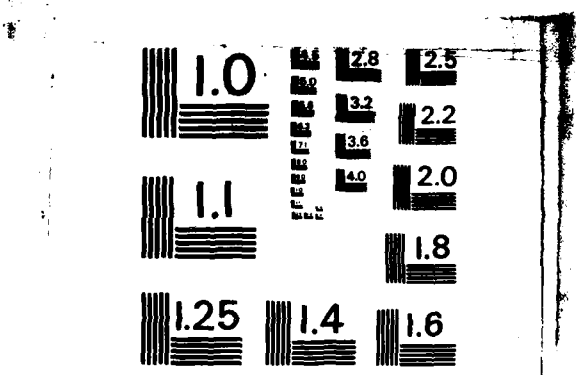

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INNER-SPHERE REORGANIZATION IN OPTICAL ELECTRON TRANSFER

by

Paul Delahay and Andrew Dziedzic

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Inner-sphere reorganization in optical electron transfer

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Free energies for photoelectron emission by aqueous solutions of hexaquo cations (V^{2+}, Cr^{2+}, Fe^{2+}), metal complexes ($Fe(CN)_6^{4-}$, $Co(NH_3)_6^{2+}$) and inorganic anions (OH^-, Cl^-, Br^-, I^-) are calculated from theory and compared with experimental threshold energies. Good agreement is obtained within the estimated error (±0.2 eV) on emission free energies. The free energy for outer-sphere reorganization is calculated from a continuous medium model. The inner-sphere reorganization energy is obtained from a bond-stretching model for hexaquo cations and metal complexes. A new method is developed for the calculation of the inner-sphere reorganization energies of univalent anions from their free energies of hydration. Reorganization free energies for electron transfer reactions ($V^{2+/3+}$, $Cr^{2+/3+}$, $Mn^{2+/3+}$, $Fe^{2+/3+}$, $Fe(CN)_6^{4-/3-}$) calculated from experimental threshold energies and computed outer-sphere reorganization free energies yield activation free energies in agreement with the values obtained from kinetic measurements. Improvements are discussed for the determination of threshold energies by extrapolation.

I. INTRODUCTION

The calculation of the free energy of reorganization of nuclear coordinates is an essential part of the theory of electron transfer reactions in solution.[1] The inner-sphere energy is generally calculated from a bond-stretching model for central ions having well defined coordination numbers, e.g., for electron transfer between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$. The outer-sphere free energy is obtained in general from the classical theory of nonequilibrium polarization of a continuous medium. The experimental

verification of the energies computed from theory ultimately rests on the agreement between calculated and experimental kinetic data for electron transfer reactions.

A very different approach was recently developed[2] in which the reorganization free energy is obtained directly from experimental results on the energetics of photoelectron emission by aqueous solutions in the 6 to 11 eV range of photon energies. The emission yield Y is measured in such experiments as a function of photon energy E, Y being defined as the number of collected electrons per incident photon. The yield is a quadratic function $(E - E_t)^2$ of E, where E_t is the threshold energy. (This relationship holds for E higher than E_t by a few tenths of an electronvolt.) The reorganization free energy R for the emission process is obtained from the experimentally determined threshold energy E_t. The quantity R thus obtained is different from the corresponding free energy for thermal electron transfer since emission involves only one species (e.g., ferrous ion) whereas electron transfer occurs between two different species (e.g., ferrous and ferric ions). There is, however, a correlation[3,4] between the reorganization free energies for the optical and thermal cases.

The application of the emission method to aqueous solutions is of general scope since most inorganic species have lower threshold energies than water (10.04±0.02 eV). The method was tested[4] by applying it to cations (V^{2+}, Cr^{2+}, Fe^{2+}) for which calculated reorganization free energies are known to yield agreement with experimental kinetic data on thermal electron transfer.

Application of the emission method to anions is of particular interest because water molecules are oriented in the electric field around anions rather than forming a definite coordination complex as with transition metal ions.[5] The distinction between inner- and outer-sphere regions can be

maintained,[6] but the bond-stretching model is no longer applicable to the inner-sphere region of anions and a new interpretation is needed. Such an interpretation, which is closely related to the treatment of the hydration energies of ions, is developed in the present paper. The validity of the emission method will be tested first on the basis of a revised equation for the energy of inner-sphere reorganization and considerably more reliable threshold energies than those previously available. Correlation between optical and thermal electron transfer processes will also be discussed.

II. FREE ENERGY OF EMISSION AND DETERMINATION OF THRESHOLD ENERGIES

The free energy ΔG_m for emission by an aqueous solution of species $A^{z+}(aq)$ is[2,4] ($z \lesssim 0$),

$$\Delta G_m = \Delta G_H + \Delta G + R + |e|\Delta\chi, \qquad (1)$$

where ΔG_H (= 4.48±0.06 eV) and ΔG are the changes of free energy for the reactions $1/2H_2(g) = H^+(aq) + e^-(g)$ and $A^{z+}(aq) + H^+(aq) = A^{(z+1)+}(aq) + 1/2H_2(g)$, respectively; R is the free energy of reorganization; e is the electronic charge and $\Delta\chi$ the difference between the surface potentials of the solution being studied and water (included in the calculated value of ΔG_H). The free energy ΔG_m can be set equal to the threshold energy E_t as will be shown below. Equation (1) therefore allows the <u>experimental</u> determination of the reorganization free energy R provided that thermodynamic data are available for the computation of ΔG. The term $|e|\Delta\chi$ for surface potentials in Eq. (1) is negligible (< 0.05 eV in absolute value in general) for this purpose.

The threshold energy E_t needed for the calculation of the free energy R is obtained by extrapolation of the square root of the yield Y against the photon energy E (Sec. I). The extrapolation is somewhat uncertain because dispersion of the solvent affects the energetics of emission[7] and actual

plots of $Y^{1/2}$ against E deviate from linearity (especially below 10 eV). Threshold energies therefore depend somewhat on the range of photon energies in which $Y^{1/2}$ is supposed to vary linearly with E. The resulting value of E_t for a given emitter varies by a few tenths of electronvolt depending on the selected range of assumed linearity. The standard deviation for a given range, however, does not exceed in general 0.01 to 0.02 eV. This uncertainty about threshold energies was greatly minimized by the analysis of data discussed in the Appendix and by considerable improvements in methodology and instrumentation.[7]

III. HEXAQUO CATIONS AND METAL COMPLEXES

A. Inner- and outer-sphere reorganization

The energy of inner-sphere reorganization U_{in} for emission is (historical background in Ref. 1),

$$U_{in} = (N/2)f_o(\Delta q_o)^2, \tag{2}$$

where N is the coordination number of the emitting species; f_o the force constant between the metal ion and the ligand for the oxidized species $A^{(z+1)+}(aq)$; Δq_o the change in the metal-ligand distance upon oxidation. Equation (2) differs from the one previously applied[4] in which the mean value of f for both reduced oxidized forms was used. The mean value of f holds for thermal electron exchange[8] in which there is reorganization about both reduced and oxidized species. There is reorganization only about the oxidized species in the optical case, and f_o must be used. This difference, which was pointed out to the authors by Sutin,[9] is significant since the use of f_o instead of the mean value of f increases U_{in} by ca. 30 percent for the cations studied in this work.

The force constant f_o is computed from the stretching frequency[10] ν_o of the oxidized species, namely $f_o = 4\pi^2\nu_o^2c^2\mu$, where c is the speed

of light in vacuum and μ is the reduced mass generally set equal to the mass of a single ligand molecule or ion.[8]

The free energy R_{out} for outer-sphere reorganization is,

$$R_{out} = (1/\epsilon_{op}^{o} - 1/\epsilon_{s})e^2/2a, \quad (3)$$

where ϵ_{op}^{o} is the limiting value of the optical constant of water in the visible range ($\epsilon_{op}^{o} = 1.777$ at 25°C), ϵ_s the static dielectric constant of water, and a the mean radius of the assumed spherical boundary between inner- and outer-sphere regions. One has[8] $a = 2a_z a_{z+1}/(a_z + a_{z+1})$, where the subscripts refer to $A^{z+}(aq)$ and $A^{(z+1)+}(aq)$, respectively. One generally sets $a = r_c + 2r_w$ for ions such as $M(H_2O)_6^{2+/3+}$, where r_c and r_w are the crystallographic radii of the ion and water ($r_w = 1.38$ Å), respectively. A thickness of the first hydration shell different from $2r_w = 2.76$ Å is recommended in Ref. 11 according to the number of coordinated water molecules, e.g., 2.19 and 2.51 Å for tetrahedral and octahedral structures, respectively. The use of this thickness increases R_{out} by ca. 0.1 eV at most for the cations of Sec. IIIB. The usual thickness of 2.76 Å was used for hydrated cations in agreement with the approach in electron transfer reactions.

B. Free energies of emission and experimental threshold energies

Experimental threshold energies corrected for dispersion (Appendix) are compared in Table I with the values of ΔG_m computed from Eq. (1) (data from Ref. 10, 12, 13). The ΔG_m-values are within ±0.2 eV because of the following sources of possible error on the terms of Eq. (1): ±0.1 eV from the uncertainty on the surface potential of water (term ΔG_H) and the neglect of $|e|\Delta\chi$; ±0.1 eV on ΔG because of possible minor complexation, hydrolysis, and departure from ideality; ±0.1 eV on R_{out} because of the uncertainty about

the thickness of the inner-sphere shell (Sec. IIIA); up to ±0.2 eV on R_{in} mostly because of the uncertainty of ±0.01 Å on Δq_o. The error on E_t for a given extrapolation range is negligible (±0.01 to ±0.02 eV, Sec. II), but some systematic error on E_t may remain even with the improved determination (Appendix) of the best extrapolation range. The systematic error on E_t should not exceed ±0.05 eV.

Agreement between the ΔG_m's and E_t's in Table I is as good as can be expected in view of the preceding error estimates. It is concluded that the energetics of photoelectron emission are understood for aqueous solutions of the hexaquo cations and metal complexes of the type in Table I. Furthermore, the free energy of emission ΔG_m can be equated to the experimental threshold energy to the approximation required for the computation of the reorganization free energy R from Eq. (1).

The contribution from R_{out} to ΔG_m in Table I is significant (ca. 1.0 eV) but does not vary much whereas ΔG and R_{in} change significantly from one ion to another. In general, threshold energies tend to be low for strong reductants such as Cr^{2+} and high for ions producing strong oxidants upon photoionization. This trend, however, can be offset by the contribution from U_{in}. Thus, Cr^{2+} and Fe^{2+} have not very different threshold energies because the difference of 1.18 eV between the ΔG's is largely compensated by the much higher U_{in} for Cr^{2+} than Fe^{2+}.

The threshold energies for V^{2+} and Cr^{2+} in Table I are higher than the previously reported values.[14] The error on the latter (6.38 and 6.14 eV) undoubtedly resulted from the uncertainty about the extrapolation range and the much higher noise level than in the present work. The threshold energy of $Fe(CN)_6^{4-}$ in Table I is higher[15] than the previous value[16] (5.5 eV) obtained from emission yields reported in Ref. 17. The reorganization free

energy for the value of E_t = 5.5 eV was judged anomalously low in Ref. 16, and emission was interpreted in terms of autoionization of a bound state. This conclusion does not seem justified in view of the higher threshold energy (6.2 eV) in Table I and the reasonable agreement with ΔG_m = 5.8 eV.

The free energy R_{out} for outer-sphere reorganization can be computed in most cases from Eq. (3) since the radius a can be estimated from crystallographic radii or by some other method. Data for the calculation of U_{in} from Eq. (2) are rather scarce, and experimental threshold energies are useful in the calculation of the inner-sphere free energy R_{in} ($R = R_{in} + R_{out}$ with $R_{in} \approx U_{in}$) from Eqs. (1) and (3) (Table II, datum from Ref. 18). Such data can be useful in estimating kinetic data for electron transfer reactions from threshold energies (Sec. IIIC). The value $R_{in} \approx 0.2 \pm 0.1$ eV for Ag^+ and Tl^+ in Table II indicates that the change Δq_o in the metal-ligand distance upon oxidation must be very low (Eq. (2)) or that emission occurs via autoionization of an excited bound state.[16]

C. Correlation with thermal electron transfer

The energetics of photoelectron emission were correlated[3,4] with the kinetics of electron transfer reactions in solution on the assumption that the mean force constant for the reactants appears in the expressions for the inner-sphere reorganization energies for the optical and thermal cases. This is only approximately the case as noted in Sec. IIIA. The correlation is then very simple.

Electron transfer reactions occur between the reduced and oxidized species of a redox couple whereas emission is observed with a solution containing only the reduced species. The energy U_{in}^x for thermal transfer therefore is twice the energy U_{in} for emission. The outer-sphere reorganization free energy R_{out}^x for thermal electron transfer is given by Eq. (3) in which

$1/2a$ is replaced by $(\frac{1}{2}a_r^{-1} + \frac{1}{2}a_o^{-1} - r_{ro}^{-1})$ where the a's pertain to the reduced and oxidized species and r_{ro} is the distance of closest approach between the centers of the reactants. Since the radii a_r and a_o are not very different, they can be set equal to the radius a of Eq. (3). Furthermore, one has $r_{ro} = a_r + a_o \approx 2a$, and consequently R^x_{out} is equal to R_{out} for emission to a good approximation. Hence,

$$\begin{aligned} R^x &= R^x_{out} + R^x_{in} \\ &= R_{out} + 2R_{in} \\ &= 2R - R_{out}. \end{aligned} \tag{4}$$

Thus, R^x can be obtained from threshold energies (Eq. (1)) and application of Eq. (3) to the calculation of R_{out}.

This treatment is approximate because the force constant f_o is applicable to the optical case (Eq. (2)) whereas the mean value $f = 2f_rf_o/(f_r + f_o)$ is valid for thermal electron transfer.[8] One has accordingly,

$$U^x_{in} = [4f_r/(f_r + f_o)]U_{in}, \tag{5}$$

instead of $U^x_{in} = 2U_{in}$ in Eq. (4). Setting $R^x_{in} \approx U^x_{in}$ one obtains,

$$\begin{aligned} R^x &= R + [(3f_r - f_o)/(f_r + f_o)]U_{in} \\ &= [4f_r/(f_r + f_o)]R - [(3f_r - f_o)/(f_r + f_o)]R_{out}, \end{aligned} \tag{6}$$

instead of Eq. (4). Equation (6) obviously recuces to (4) for $f_r = f_o$. The difference is significant, e.g., $R^x = 1.52R - 0.52R_{out}$ for $f_r = 1.6 \times 10^5$ and $f_o = 2.6 \times 10^5$ dyne cm^{-1} instead of Eq. (4).

The reorganization free energy R^x is related to the free energy of activation $\Delta G^{\neq}$ for electron transfer in solution involving no change of free energy by the relationship[19,20]

$$\Delta G^{\neq} = R^x/4 + w, \tag{7}$$

where w is the work required to bring from infinity in solution the two reactants together in the precursor state. The term w is generally minor (ca. 0.05 eV). Equation (7) is approximate[1,8] but suffices for our present purpose.

Values of R^x and $\Delta G^{\neq}$ from Eqs. (6) and (7) are compared in Table III with the free energies of activation deduced from kinetic data.[21] The experimental value of $\Delta G^{\neq}$ for Mn^{2+} was obtained from the Marcus cross relationship and is very approximate. These results show that rather good estimates of R^x can be obtained from threshold energies and Eqs. (3) and (6) without data on the change Δq_o in the metal-ligand distance (Eq. (2)). This may prove useful in the study of unstable redox couples in solution.

IV. ANIONS

A. Correlation between inner-sphere reorganization and ionic hydration

We consider photoelectron emission by aqueous solutions of univalent anions $A^-(aq)$. This process is the opposite of the hydration of the ion $A^-(g)$ except that the negative charge is removed from solution by the electron and the hydrated atom or radical A(aq) is left in solution in the emission process. There is therefore a close correlation between the free energies of hydration (ΔG_s) and inner-sphere reorganization (R_{in}). This correlation will be established.

The hydration free energy can be written as the following sum[11]:

$$\Delta G_s = \Delta G_{cav} + \Delta G_B + U(ep) + U(ep_\alpha) + U(pp) + U(p_\alpha p) + U(eq) + U(pq) + U(p_\alpha q) + U(qq) + U_{disp}(A^-w) + U_{disp}(ww) + U_{rep} + \Delta G_v + \Delta G_{st}. \quad (8)$$

Notations are as follows: ΔG_{cav} the free energy for formation of the ionic cavity in the liquid with breaking up of the liquid water structure around the ion; ΔG_B the free energy for Born charging beyond the inner-sphere boundary;

terms such as U(ep) representing the interaction energies involving the ionic charge (e), water dipoles (p), water induced dipoles (p_α), water quadrupoles (q); $U_{disp}(A^-w)$ and $U_{disp}(ww)$ the ion-water and water-water dispersion energies; U_{rep} the energy for ion-water and water-water repulsion; ΔG_v the free energy for the change of volume of the liquid resulting from ionic hydration; ΔG_{st} a correction for reference to the standard state. The energies for induced dipole-induced dipole interaction and the formation of induced dipoles which are included in the expression for ΔG_s in Ref. 11 were deleted in Eq. (8) since these terms should cancel out according to Ref. 22.

The following terms in Eq. (8) do not pertain to inner-sphere reorganization: ΔG_B, since Born charging is taken into account separately in emission by the introduction of the outer-sphere reorganization free energy; $U(ep_\alpha)$, which accounts for an interaction involving no change in nuclear configuration; the difference of dispersion energies,

$$\Delta U_{disp} = U_{disp}(A^-w)\Big|_{r_o} - U_{disp}(Aw)\Big|_{r_o}, \tag{9}$$

where both terms are calculated for the nuclear configuration of the hydrated ion $A^-(aq)$ (denoted by the subscript r_o). The other terms in Eq. (8) are the same in absolute value for ΔG_s and R_{in}.

The free energy R_{in} (> 0) is,

$$R_{in} = -[\Delta G_s - \Delta G_B - U(ep_\alpha) - \Delta U_{disp} + \Delta G_n], \tag{10}$$

where ΔG_n is the hydration free energy of the atom or radical A(g). This term accounts for the formation of the hydrated species A(aq) in emission.

B. Calculation of the inner-sphere reorganization free energy from the hydration free energy

Expressions will be given for the terms of Eq. (10). The Born free energy is,

$$\Delta G_B = -(1 - \varepsilon_s^{-1})e^2/2a, \tag{11}$$

where the radius $a = r_c + 2r_w = r_c + 2.76$ (Å) (Sec. IIIA). The energy $U(ep_\alpha)$ for charge-induced dipole interaction is,

$$U(ep_\alpha) = - Nep_\alpha/r_o^2, \tag{12}$$

where N is the number of water molecules in the inner-sphere shell, p_α is the induced dipole, and $r_o = r_c + r_w$ on the assumption that the center of the induced dipole is at the distance $r_c + r_w$ from the charge. One has,[6]

$$p_\alpha = (1/2)\alpha e/r_o^2, \tag{13}$$

where α ($= 1.444 \times 10^{-24}$ cm^3) is the polarizability of the water molecule. The dispersion energies in Eq. (9) are of the form

$$U_{disp} = - (3N/2)[II'/(I + I')]\alpha\alpha'/r_o^6, \tag{14}$$

where I and I' are the ionization energies of water and the ion $A^-(g)$ or radical A(g), respectively, and α' is the polarizability of $A^-(g)$ or A(g).

Values of R_{in} computed from Eqs. (9) to (14) for N = 4 (OH^-) and 6 (halides) are listed in Table IV (data from Ref. 23 to 30). The choice of N = 6 for the halides is supported by the recent neutron diffraction determination[31] of N = 6.2±0.4 for Cl^-. The vibrational contribution to R_{in} for OH^- was neglected since the O–H interatomic distance is the same[32] within 0.002 Å for the ion $OH^-(g)$ and the radical OH(g). It is concluded that, to a first approximation, inner-sphere reorganization of the univalent anions studied in this work is equivalent to the inverse of hydration except for Born charging and charge-induced dipole interaction.

The R_{in} values from Table IV were used to compute the emission free energies ΔG_m listed in Table V (data from Ref. 33 and 34). The hydration free energy ΔG_n of A(g) in Eq. (10) was eliminated by introducing $\Delta G - \Delta G_n$ and $R + \Delta G_n = R_{out} + R_{in} + \Delta G_n$ in Eq. (1). The quantity $\Delta G - \Delta G_n$ is the change of free energy for the reaction, $A^-(aq) + H^+(aq) = A(g) + 1/2H_2(g)$, for which accurate thermodynamic data are available in the present case. The

use of approximate data[30] on ΔG_n is avoided in this way. The values of ΔG_m in Table V include the contribution from the surface potential of pure water (cf. discussion of Eq. (1)). The agreement between the ΔG_m's and the experimental threshold energies for anions is comparable to the agreement achieved for cations in Table I. The threshold energy for F^- could not be determined since ΔG_m is higher by ca. 0.6 eV than $E_t = 10.04 \pm 0.02$ eV for liquid water.

The free energy R_{in} was also calculated by considering the terms in Eq. (8) for ΔG_s which do not appear in Eq. (10). This approach which does not make use of the experimental hydration free energy ΔG_s is much more demanding of the model than the application of Eq. (10). Molecular dynamics simulation calculations[35] show that distribution functions must be introduced for the orientation of water molecules about the anion. Calculations for the halides based on the simple expressions of Ref. 11 for the U-terms of Eq. (8) showed that the dominant terms in R_{in} are the free energy for ionic cavity formation, the charge-dipole energy, the charge-quadrupole energy and the repulsion energy.

CONCLUSION

Three main conclusions are reached. (i) Calculated free energies of emission (±0.2 eV estimated error) are in good agreement with experimental threshold energies for metal hexaquo cations and complexes and inorganic anions. (ii) The calculation of inner-sphere reorganization energies of univalent anions from hydration free energies developed in the present paper yields values agreeing with experiment. (iii) Reorganization free energies for electron transfer reactions calculated from experimental threshold energies and computed outer-sphere reorganization free energies yield activation free energies in agreement with experimental values.

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APPENDIX

Threshold energies were obtained by the following extrapolation procedure: The derivative $dY^{1/2}/dE$ was computed as a function of E by digital processing and differentiation by means of Savitzky-Golay filters.[36-39] The derivative $dY^{1/2}dE$ would be independent of E if the quadratic emission law $(E - E_t)^2$ held rigorously. Actually, there is a dispersion correction ΔG_d to the free energy of emission because electron transfer is observed at a photon energy at which the optical dielectric constant of the solvent is different from the limiting value ϵ_{op}^o in the visible range ($\epsilon_{op}^o = 1.777$ for water at 25°C). One has,

$$\Delta G_d = K[1/\epsilon_{op}^o - \epsilon_1/(\epsilon_1^2 + \epsilon_2^2)], \tag{15}$$

where ϵ_1 and ϵ_2 are respectively the real and imaginary parts of the dielectric constant of water at the photon energy E, and K is a constant for a given ion. The value of K is derived in Ref. 7, but K in fact was obtained by a fitting procedure described below. Thus, the value of E_t in $(E - E_t)^2$ depends on the value of E at which Y is measured, and consequently $dY^{1/2}/dE$ varies with E and extrapolation of $Y^{1/2}$ to $Y^{1/2} = 0$ is uncertain.

Dispersion was corrected for by shifting each point representing $Y^{1/2}$ along the E-scale toward lower photon energies by the value of ΔG_d calculated for a given K and the prevailing experimental values of ϵ_1 and ϵ_2 obtained

from reflectance spectroscopic data on liquid water.[40] The resulting plot of shifted $Y^{1/2}$ points against E is corrected for dispersion for the proper value of K. The latter was determined by minimizing the standard deviation of $dY^{1/2}/dE$ about its mean value in a given interval of photon energies (ca. 1 eV). Dispersion corrections to E_t are rather small (< 0.1 eV in absolute value), but the preceding procedure is very useful in ascertaining the proper range for linear extrapolation to $Y^{1/2} = 0$.

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Table I. Calculated free energies of emission of cations and metal complexes versus experimental threshold energies

	ΔG (eV)	U_{in} [a] (eV)	R_{out} [b] (eV)	ΔG_m [c] (eV)	E_t [d] (eV)
V^{2+} (0.5 M)	-0.25	1.07	1.15	6.5	6.82
Cr^{2+} (1 M)	-0.41	1.91	1.15	7.1	7.06
Fe^{2+} (1 M)	0.77	0.94	1.14	7.3	7.30
$Fe(CN)_6^{4-}$ (0.2 M)	0.36	0.05	0.9	5.8	6.2
$Co(NH_3)_6^{2+}$ (0.2 M)	0.1	2.24	1.18	8.0	7.8

[a] Computed for N = 6; $f_o = 2.55 \times 10^5$ dyne cm^{-1} for V^{2+}, Cr^{2+}, Fe^{2+} obtained from[10] $\nu_o = 490$ cm^{-1}; $f_o = 4.00 \times 10^5$ dyne cm^{-1} for $Fe(CN)_6^{4-}$ from[10] $\nu_o = 511$ cm^{-1}; $f_o = 2.48 \times 10^5$ dyne cm^{-1} for $Co(NH_3)_6^{2+}$ from[10] $\nu_o = 498$ cm^{-1}; $\Delta q_o = 0.15$ (V^{2+}) from Ref. 12, 0.20 (Cr^{2+}), 0.14 (Fe^{2+}), 0.026 ($Fe(CN)_6^{4-}$), 0.22 Å ($Co(NH_3)_6^{2+}$) from Ref. 13.

[b] Computed for a = 3.48 (V^{2+}, Cr^{2+}), 3.51 (Fe^{2+}), 4.5 ($Fe(CN)_6^{4-}$), 3.35 Å ($Co(NH_3)_6^{2+}$), .

[c] ±0.2 eV estimated error (see text).

[d] ±0.05 eV possible systematic error from extrapolation (see text).

Table II. Free energies R_{in} of inner-sphere reorganization of cations calculated from threshold energies

	E_t (eV)	ΔG[a] (eV)	R_{out}[b] (eV)	R_{in}[c] (eV)
Ag^+ (1 M)	7.67	2.00	1.0	0.2
Tl^+ (1 M)	7.85	2.2	1.0	0.2
Mn^{2+} (1 M)	7.95	1.56	1.11	0.8

[a] From Ref. 18 for Tl^+/Tl^{2+}.

[b] Computed for a = 4.0, 4.1, 3.56 Å, respectively.

[c] Estimated error of ±0.2 eV from the uncertainty on E_t, ΔG and R_{out}.

Table III. Activation free energies for electron transfer reactions calculated from threshold energies versus experimental values

	R^a (eV)	$R^{x\ b}$ (eV)	w^c (eV)	$\Delta G^{\neq}_{calc}$ (eV)	$\Delta G^{\neq}_{exp}$ [d] (eV)
V^{2+} (0.5 M)	2.59	3.38	0.04	0.88	0.87
Cr^{2+} (1 M)	2.99	4.00	0.05	1.05	1.03
Mn^{2+} (1 M)	1.91	2.36	0.03	0.62	(0.75)
Fe^{2+} (1 M)	2.05	2.55	0.06	0.70	0.69
$Fe(CN)_6^{4-}$ (0.2 M)	1.36	1.95	0.04	0.53	0.47

[a] From Eq. (1) and data in Tables I and II.

[b] From Eq. (6) and R_{out} values from Tables I and II. f_r = 1.61, 1.61, 1.66, 1.61, 5.24×10^5 dyne cm^{-1}; $f_o = 2.55 \times 10^5$ dyne cm^{-1} for four cations and 4.00×10^5 dyne cm^{-1} for $Fe(CN)_6^{4-}$. Estimated error, ±0.15 eV.

[c] From Ref. 3.

[d] From Ref. 21. Value for Mn^{2+} from Marcus cross relationship.

Table IV. Calculated free energies of inner-sphere reorganization of anions

	r_c [a] (Å)	$-\Delta G_s$ [b] (eV)	$-\Delta G_{\beta}$ (eV)	$-U(ep_{\alpha})$ (eV)	ΔU_{disp} [c] (eV)	ΔG_n [d] (eV)	R_{in} (eV)
F^-	1.36	4.50	1.73	1.11	0.06	0.1	1.62
Cl^-	1.81	3.30	1.56	0.60	0.08	0.11	1.11
Br^-	1.95	3.00	1.51	0.51	0.07	0.09	0.96
I^-	2.16	2.61	1.44	0.40	0.05	0.13	0.69
OH^-	1.47	3.93	1.68	0.63	-	-0.09	1.71

[a] From Ref. 23.

[b] From Ref. 24 for F^- and OH^- and Ref. 25 for Cl^-, Br^-, I^-.

[c] Values of I and I' from Ref. 26 and 27; α'-values from Ref. 28 for $A^-(g)$ and from Ref. 29 for A(g).

[d] From Ref. 30. ±0.04 to ±0.1 eV uncertainty on these values of ΔG_n.

Table V. Calculated free energies of emission of anions versus experimental threshold energies

	$\Delta G - \Delta G_n$ [a] (eV)	R_{out} (eV)	$R_{in} + \Delta G_n$ (eV)	ΔG_m (eV)	E_t [b] (eV)
F^-	3.48	0.96	1.72	10.6	-
Cl^-	2.45	0.87	1.22	9.0	9.00
Br^-	1.92	0.84	1.05	8.3	8.15
I^-	1.26	0.80	0.82	7.4	7.43
OH^-	1.89	0.94	1.62	8.9	8.59

[a] From Ref. 33 except for OH^- (Ref. 34).

[b] ± 0.05 eV possible systematic error on E_t. 1 M solutions.

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